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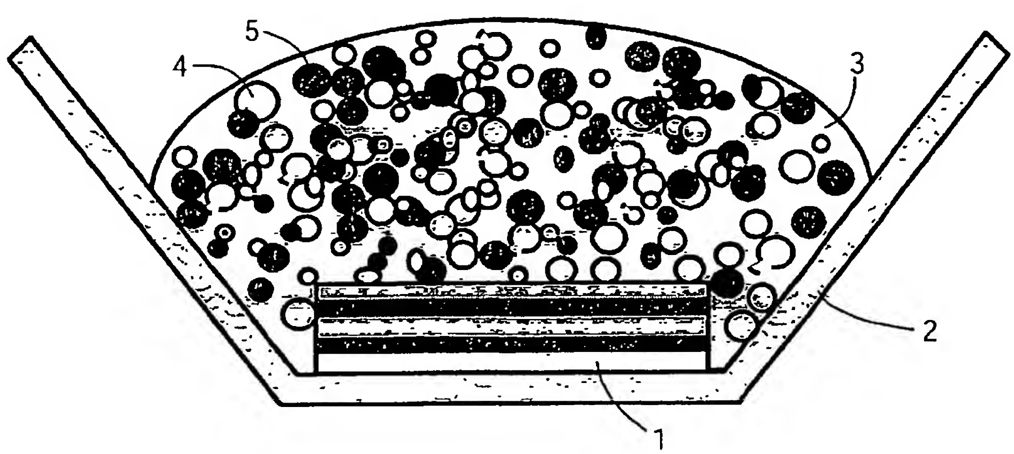
(54) Title: TRI-COLOR WHITE LIGHT LED LAMP



(57) Abstract: The invention relates to a tri-color lamp for generating white light comprising a phosphor composition comprising a phosphor of general formula $(Ba_{1-x-y-z}Sr_xCa_y)_2SiO_4:Eu_z$, wherein $0 \leq x \leq 1$, $0 \leq y \leq 1$ and $0 < z < 1$. The phosphor composition may also comprise a red phosphor. The two phosphors can absorb radiation emitted by a light emitting diode, particularly a blue LED. This arrangement provides a mixing of three light sources -light emitted from the two phosphors and unabsorbed light from the LED. The invention also relates to an alternative to a green LED comprising a single green phosphor of general formula $(Ba_{1-x-y-z}Sr_xCa_y)_2SiO_4:Eu_z$, wherein $0 \leq x \leq 1$, $0 \leq y \leq 1$ and $0 < z < 1$, that absorbs radiation from a blue LED. A resulting device provides green light of high absorption efficiency and high luminous equivalent values.

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Tri-color white light LED lamp

FIELD OF INVENTION

The present invention relates to a tri-color lamp. The lamp comprises a phosphor composition and a light emitting diode for an excitation energy source. In particular, the lamp employs a blue LED and a mixture of red and green phosphors for the production of white light.

BACKGROUND OF THE INVENTION

There is an ongoing need to generate new phosphor compositions to improve efficiency and color quality in luminescent devices, particularly in the production of white light. Phosphors are luminescent materials that can absorb an excitation energy (usually radiation energy) and store this energy for a period of time. The stored energy is then emitted as radiation of a different energy than the initial excitation energy. For example, "down-conversion" refers to a situation where the emitted radiation has less quantum energy than the initial excitation radiation. Thus, the energy wavelength effectively increases, and this increase is termed a "Stokes shift". "Up-conversion" refers to a situation where the emitted radiation has greater quantum energy than the excitation radiation (" Anti-Stokes shift").

Improvements in efficiency and color quality in phosphor-based devices are constantly being developed. "Efficiency" relates to the fraction of photons emitted with respect to a number of photons initially provided as excitation energy. Inefficient conversion results when at least a portion of the energy is consumed by non-radiative processes. Color "quality" can be measured by a number of different rating systems. "Chromaticity" defines color by hue and saturation. "CIE" is a chromaticity coordinate system developed by Commission Internationale de l'Eclairage (International commission on illumination). The CIE Chromaticity Coordinates are coordinates that define a color in "1931 CIE" color space. These coordinates are defined as x, y, z and are ratios of the three standard primary colors, X, Y, Z (tristimulus values), in relation to the sum of the three tristimulus values. A CIE chart contains a plot of the x, y and z ratios of the tristimulus values versus their sum. In the situation where the reduced coordinates x, y, z add to 1, typically, a two-dimensional CIE (x, y) plot is used.

White-like colors can be described by a "correlated color temperature" (CCT). For example, when a metal is heated, a resulting light is emitted which initially glows as a red color. As the metal is heated to increasingly higher temperatures, the emitted light shifts to higher quantum energies, beginning with reddish light and shifting to white light and ultimately to a bluish-white light. A system was developed to determine these color changes on a standard object known as a blackbody radiator. Depending on the temperature, the blackbody radiator will emit white-like radiation. The color of this white-like radiation can then be described in the CIE chromaticity chart. Thus, the correlated color temperature of a light source to be evaluated is the temperature at which the blackbody radiator produces the chromaticity most similar to that of the light source. Color temperature and CCT are expressed in degrees Kelvin.

A "color rendering index" (CRI) is established by a visual experiment. The correlated color temperature of a light source to be evaluated is determined. Then eight standard color samples are illuminated first by the light source and then by a light from a blackbody having the same color temperature. If a standard color sample does not change color, then the light source has a theoretically perfect special CRI value of 100. A general color rendering index is termed "Ra", which is an average of the CRIs of all eight standard color samples.

Older white lamps involved emission of light over a broad wavelength range. It was then discovered that a white-like color can be simulated by a mixture of two or three different light colors, where each emission comprised a relatively narrow wavelength range. These lamps afforded more control to manipulate the white color because emissive properties (emission energy and intensity) of the individual red, green and blue light sources can be individually tailored. This method thus provided the possibility of achieving improved color rendering properties.

An example of a two-color lamp comprises one phosphor and an excitation energy source. Light emitted by the phosphor combines with unabsorbed light from the excitation source to produce a white-like color. Further improvements in fluorescent lamps involved three different light colors (i.e. a tri-color lamp) resulting in white light at higher efficiencies. One example of a tri-color lamp involved blue, red and green light-emitting phosphors. Other previous tri-color lamps comprised a combination of light from two phosphors (a green and red phosphor) and unabsorbed light from a mercury plasma excitation source.

Previous tri-color lamps involving a mercury plasma excitation source, however, suffer many disadvantages including: (1) a need for high voltages which can result in gaseous discharge with energetic ions; (2) emission of high energy UV quanta; and (3) correspondingly low lifetimes. Thus, there is an ongoing need for devices that overcome these deficiencies.

WO 01/24229 discloses to a tri-color lamp for generating white light. In particular, WO 01/24229 relates to a phosphor mixture comprising two phosphors having host sulfide materials that can absorb radiation emitted by a light emitting diode, particularly a blue LED. This arrangement provides a mixing of three light sources -light emitted from the two rare earth ion, to allow matching of the phosphors in relation to the LED emitted radiation. Power fractions of each of the light sources can be varied to achieve good color rendering. WO 01/24229 also relates to an alternative to a green LED comprising a single green phosphor that absorbs radiation from a blue LED. A resulting device provides green light of high absorption efficiency and high luminous equivalent values.

There remains a continued challenge to uncover phosphor compositions and mixtures of these compositions to provide improved properties, including improved efficiency, color rendering (e.g. as measured by high color rendering indices) and luminance (intensity), particularly in a tri-color, white lamp.

It has been observed that photoluminescent phosphor compounds have characteristic ranges of luminescent quenching temperatures. That is, when the phosphor is excited into luminescence as for example by subjecting the same to radiation from a source of ultraviolet light, the intensity of the luminescence will gradually decrease as the temperature of the phosphor is raised through a specified range of temperatures. For example, the compound Zn.80 Cd.20 S : AgCl will gradually quench from bright green, to dull green, to green gray, to gray, to black, as the temperature is increased from 95 °C to 105 °C. The temperature ranges of the compounds provided by the afore described basic phosphor system are found to be determined by the composition of their anionic component. Phosphor compounds may be therefore made to have different quenching temperature ranges as well as different color characteristics. The thermal quenching at higher temperatures reduces the LED efficiency, in particular at high chip temperatures. Therefore it is desirable to replace sulfide phosphors by non –sulfide phosphors with a higher thermal quenching temperature.

SUMMARY OF THE INVENTION

One aspect of the present invention provides a device comprising a light emitting diode, for emitting a pattern of light. The device further comprises a phosphor composition comprising a phosphor of general formula $(Ba_{1-x-y-z}Sr_xCa_y)_2SiO_4:Eu_z$, wherein $0 \leq x \leq 1$, $0 \leq y \leq 1$ and $0 < z < 1$.

The phosphor comprises as a host an alkaline earth silicate lattice and divalent Europium as a dopant and the composition is positioned in the light pattern.

Such a device shows high efficiency, particularly at chip temperature above 150°C, because of the high quenching temperature of such a phosphor.

Especially, when the phosphor is comprised in a thin film layer the high quenching temperature of the phosphor is of advantage.

Another aspect of the present invention provides a light emitting device comprising a LED for emitting a pattern of light and a phosphor composition comprising a mixture of a first phosphor and a second phosphor. The first phosphor has the general formula $(Ba_{1-x-y-z}Sr_xCa_y)_2SiO_4:Eu_z$, wherein $0 \leq x \leq 1$, $0 \leq y \leq 1$ and $0 < z < 1$ and comprises a host alkaline earth silicate lattice and divalent Europium as a dopant and is capable of being excited by a light emitting diode. The second phosphor is a red-emitting phosphor.

Another aspect of the present invention provides a light emitting device wherein the phosphor composition comprises a green phosphor of general formula $(Ba_{1-x-y-z}Sr_xCa_y)_2SiO_4:Eu_z$, wherein $0 \leq x \leq 1$, $0 \leq y \leq 1$ and $0 < z < 1$, and a red phosphor, wherein the red phosphor is selected from the group of $(Sr_{1-x-y}Ba_xCa_y)S:Eu$ wherein:
$0 \leq x < 1$ and $0 \leq y < 1$;
$CaS:Ce,Cl$; $Li_2Sr\ SiO_4:Eu$; $(Sr_{1-x}Ca_x)SiO_4:Eu$ wherein $0 \leq x < 1$;
$(Y_{1-x}Gd_x)_3(Al_{1-y}Ga_y)_5O_{12}:Ce$ wherein $0 \leq x < 1$ and $0 \leq y < 1$ and
$(Sr_{1-x-y}Ba_xCa_y)_2Si_5N_8:Eu$ wherein $0 \leq x < 1$ and $0 \leq y < 1$. The emission spectrum of such a phosphor composition has the appropriate wavelengths to obtain together with the blue light of the LED a high quality white light with good color rendering at the required color temperature.

Another aspect of the present invention provides a phosphor composition comprising a phosphor of general formula $(Ba_{1-x-y-z}Sr_xCa_y)_2SiO_4:Eu_z$, wherein $0 \leq x \leq 1$, $0 \leq y \leq 1$ and $0 < z < 1$ and comprising a host alkaline earth silicate lattice and divalent Europium as a dopant. A phosphor of general formula $(Ba_{1-x-y-z}Sr_xCa_y)_2SiO_4:Eu_z$, wherein $0 \leq x \leq 1$, $0 \leq y \leq 1$ and $0 < z < 1$ absorbs photons efficiently, especially photons of a

blue LED operating at 450 nm and shows high quantum efficiency upon excitation of such wavelength. Such phosphor shows high quenching temperature of TQ 50 % at 230°C.

Other advantages, novel features, and objects of the invention will become apparent from the following detailed description of the invention when considered in conjunction with the accompanying drawings, which are schematic and which are not intended to be drawn to scale. In the figures, each identical or nearly identical component that is illustrated in various figures is represented by a single numeral. For the purposes of clarity, not every component is labeled in every figure, nor is every component of each embodiment of the invention shown where illustration is not necessary to allow those of ordinary skill in the art to understand the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows a schematic of a tri-color lamp comprising a two-phosphor mixture of $(Ba_{0.49}Sr_{0.49})_2SiO_4:Eu_{0.02}$ and $Sr_2Si_5N_8:Eu$ positioned in a pathway of light emitted by an LED.

Fig. 2 shows an overlay of emission and excitation spectrum of $(Ba_{0.49}Sr_{0.49})_2SiO_4:Eu_{0.02}$ upon excitation by a blue LED at 460 nm;

Fig. 3 shows a simulation of spectra of a mixture of $(Ba_{0.49}Sr_{0.49})_2SiO_4:Eu_{0.02}$ and $Sr_2Si_5N_8:Eu$ upon excitation by a blue LED at 450 nm at different color temperatures; and

Fig. 4 shows spectra of LEDs comprising a mixture of $(Ba_{0.49}Sr_{0.49})_2SiO_4:Eu_{0.02}$ and SrS:Eu and a blue LED emitting at 450 nm at different color temperatures;

Fig. 5 shows the reflection spectra of $(Ba_{0.49}Sr_{0.49})_2SiO_4:Eu_{0.02}$ without an SiO_2 coating and with an SiO_2 coating.

DETAILED DESCRIPTION

The invention relates, in part to the discovery that a tri-color lamp employing specific green and red phosphors excitable by a common light emitting diode (LED) can achieve white light at higher efficiencies with superior color rendering over previous fluorescent lamps and are not apt to substantial quenching at chip temperature above 150 °C and up to 230°C.

An advantageous feature of the present invention involves the use of an LED as an excitation source. An LED has a p-n junction between doped semiconductor regions.

Upon application of a current, there can exist sufficient energy to allow electrons and holes to cross the p-n junction such that a resulting recombination of electrons and holes causes emission of radiation. Advantages of LEDs over other excitation energy sources include small size, low power consumption, long lifetimes and low amounts of thermal energy emitted. In addition, LEDs have small dimensions that allow miniaturization of devices.

In one embodiment, the common LED is a blue LED. The use of blue light as an excitation radiation over other light sources has been found to be particularly advantageous in that conversion efficiency to visible light is higher. In one embodiment each phosphor is capable of being excited by a common LED which emits radiation at a wavelength from about 450 nm to about 480 nm. It has been found that color rendering can decrease at excitation energies below 450 nm whereas absorption by the phosphors decreases at excitation energies greater than 480 nm. An example of a blue LED that emits radiation in the above-mentioned energy ranges is a (In,Ga)N diode.

A blue light source can provide inherent advantages over UV excitation sources in that power efficiency is increased for red and green phosphors excited by blue light. The present phosphor materials generally require lesser Stokes shifts than phosphors of the previous devices. For example, certain tri-color prior art fluorescent lamps incorporate mercury plasmas which provide a UV emission centered at approximately 4.9 eV. This UV light excites blue, red and green phosphors such that resulting emission spectra show maximum intensities at energies of approximately 2.8 eV (unabsorbed light), 2.3 eV (green) and 2.0 eV (red) respectively. Significant Stokes shifts are obviously involved in this situation. Power efficiency, however, is limited by quantum deficit, which is the difference of the quantum energies of exciting and emitted quanta. Thus, for the example described above, power efficiency of the green light is, on average, (4.9 eV-2.3 eV)/4.9 eV = 53%. In contrast, green (2.3 eV) and red {2.0 eV) phosphors excited by a blue LED with an emission of about 2.7 e V (~460 nm) exhibit smaller Stokes shifts and quantum deficits, and accordingly power efficiency is greater .

Phosphors comprise a host lattice and dopant ions. Typically, the host material has an inorganic, ionic lattice structure (a "host lattice") in which the dopant ion replaces a lattice ion. The dopant is capable of emitting light upon absorbing excitation radiation. Ideal dopants strongly absorb excitation radiation and efficiently convert this energy into emitted radiation. If the dopant is a rare earth ion, its absorb and emits radiation via 4f-4f transitions, i.e. electronic transitions involving f-orbital energy levels. While f-f transitions are quantum-mechanically forbidden resulting in weak emission intensities, it is known that certain rare

earth ions, such as divalent Europium strongly absorb radiation through allowed 4f-5df transitions (via d- orbital/f-orbital mixing) and consequently produce high emission intensities.

The emissions of rare earth dopants, such as divalent Europium can be shifted in energy depending on the host lattice in which the dopant ion resides. Thus, this aspect of the invention lies, in part, in the discovery that certain rare earth dopants efficiently convert blue light to visible light when incorporated into an appropriate host material. The phosphor according to the invention comprises a host lattice, which is a earth alkaline silicate, i.e. a lattice which includes silicate and earth alkaline metal ions.

Another advantageous feature of the present invention is to provide a phosphor mixture excitable by one common blue energy source of a relatively narrow linewidth emit light at two different energy ranges (e.g. red and green). Strategies to provide appropriate phosphors are disclosed here. In one embodiment, the dopant is the same in the first and second phosphor. The red and green emissions of the two phosphors can be tuned by selecting an appropriate host material.. The red phosphor is selected from the group consisting of $(Sr_{1-x-y}Ba_xCa_y)S$:Eu wherein $0 \leq x < 1$ and $0 \leq y < 1$; CaS:Ce,Cl; $Li_2Sr\,SiO_4$:Eu; $(Sr_{1-x}Ca_x)SiO_4$:Eu wherein $0 \leq x < 1$; $(Y_{1-x}Gd_x)_3(Al_{1-y}Ga_y)_5O_{12}$:Ce wherein $0 \leq x < 1$ and $0 \leq y < 1$ and $(Sr_{1-x-y}Ba_xCa_y)_2Si_5N_8$:Eu wherein $0 \leq x < 1$ and $0 \leq y < 1$.

Fig. 2 is an overlay of emission spectra from two different phosphors i.e. $(Ba_{0.49}Sr_{0.49})_2SiO_4:Eu_{0.02}$ and $Sr_2Si_5N_8$:Eu being excited by one common {In,Ga)N LED at 450 nm. The phosphors are provided as a mixture in an encapsulant. The spectra have been normalized to an intensity of unity.

Fig. 3 is an overlay of emission spectra from two different phosphors i.e. $(Ba_{0.49}Sr_{0.49})_2SiO_4:Eu_{0.02}$ and SrS:Eu being excited by one common {In,Ga)N LED at 450 nm. The phosphors are provided as a mixture in an encapsulant. The spectra have been normalized to an intensity of unity.

Preferably the amount of dopant present in the host lattice is from 0.01 mol% to 8 mol%.

In the operation of the embodiment of the present invention radiation of ultraviolet rays from the LED chip onto the phosphor layer excites the phosphors and produces a bright and uniform luminescence over the entire surface off the layer.

In one embodiment, the device is a lamp. In one embodiment, the lamp emits white light. In this embodiment, the first phosphor is a green phosphor of general formula $(Ba_{0.49}Sr_{0.49})_2SiO_4:Eu_{0.02}$ and the second phosphor is a red phosphor of general formula

$Sr_2Si_5N_8$:E, where the white color is achieved by effectively mixing the green and red light with unabsorbed blue light provided by the LED.

The white light lamp of the present invention is particularly advantageous in that the color rendering properties are far superior to those of any previous white lamps. In one embodiment, the lamp is capable of emitting radiation having a color rendering index, Ra of at least about 60 at a color temperature from about 2700 K to about 8000 K, preferably an Ra of at least about 70, more preferably an Ra of at least about 80 and even more preferably an Ra of at least about 90. In a preferred embodiment, the lamp generates a CRI, Ra of greater than 70 for CCT values of less than 6000 K.

Fig. 2 shows a simulation of emission spectra of a tri-color lamp comprising a mixture of $(Ba_{0.49}Sr_{0.49})_2SiO_4:Eu_{0.02}$ and $Sr_2Si_5N_8$:Eu excited by a blue (In,Ga)N LED at 460 nm. Emission intensity or radiance is indicated in the ordinate axis. This system exhibits superior color rendering properties over a wide range of color temperatures. It is a feature of the present invention to mix respective amounts of the phosphors and to illuminate these phosphors with a blue LED to closely match these desired simulated spectra.

By varying optical properties of each source of light in the device, the device can be designed to have desired characteristics depending on a particular application. For example, certain devices may be required to generate light of high intensity and only adequate color rendering is needed, whereas other applications may require high color rendering properties, at the expense of efficiency. Alternatively, color rendering can be sacrificed for higher efficiency. For example, a 50% increase in efficiency can be achieved by decreasing Ra down to about 60. Such properties can be varied by changing relative power fractions of each light source. A "power fraction" is the fraction of light from each source that provides the final light color. Power fractions can be varied by, for example, changing a relative amount of phosphor material present in the device or varying dopant concentration.

It is understood that the phosphor composition can comprise more than two phosphors so long as optimal color rendering properties are achieved.

In one embodiment, the device further comprises a polymer for encapsulating the phosphor composition. In this embodiment, the phosphor mixture should exhibit high stability properties in the encapsulant. Preferably, the polymer is optically clear to prevent significant light scattering. In one embodiment, the polymer is selected from the group consisting of epoxy and silicone resins. A variety of polymers are known in the LED industry for making 5 mm LED lamps. Encapsulation can be performed by adding the phosphor

mixture to a liquid that is a polymer precursor. For example, the phosphor mixture can be a powder. Introducing phosphor particles into a polymer precursor liquid results in formation of a slurry (i.e. a suspension of particles). Upon polymerization, the phosphor mixture is fixed rigidly in place by the encapsulation. In one embodiment, both the composition and the LED are encapsulated in the polymer.

The use of phosphors with general formula $(Ba_{1-x-y-z}Sr_xCa_y)_2SiO_4:Eu_z$, wherein $0 \leq x \leq 1$, $0 \leq y \leq 1$ and $0 < z < 1$ is especially advantageous if the phosphor composition is applied as a thin film or in a small volume, because they are not sensitive to higher temperatures, which result in thin layers due to heat generated by the Stokes shift together with strong absorption and consequently very small light penetration depth.

The phosphor comprising composition may be fabricated by eventually dry blending phosphors in a suitable blender and then assign to a liquid suspension medium or the individual phosphor or phosphors may be added to a liquid suspension, such as the nitrocellulose/butylacetate binder and solvent solution used in commercial lacquers. Many other liquids including water with a suitable dispersant and thickener or binder such as polyethylene oxide can be used. The phosphor containing composition is painted or coated or otherwise applied on the LED and dried.

Otherwise the phosphor or phosphors can be combined with a suitable polymer system, such as polypropylene, polycarbonate, or polytetrafluoroethylene, to a phosphor composition, which is then coated or applied to the LED and dried, solidifies, hardeners, or cured. The liquid polymer system may optionally be UV cured or room temperature cured to minimize any heat damage to the LED.

Otherwise a clear polymer lens made of suitable plastic such as polycarbonate or other rigid transparent plastic is molded over the LED. Lens may be further coated with anti-reflective layers to facilitate light to escape the device.

Although the role of phosphor grain size (mean diameter of phosphor particles) is not completely understood, weight fractions may change depending on a particular grain size. Preferably, grain sizes are less than 15 µm, and more preferably, less than 12 µm, to avoid clogging of devices which dispose the phosphors. In one embodiment, the grain size of each phosphor type varies. In certain specific embodiments, the grain size of $(Ba_{1-x-y-z}Sr_xCa_y)_2SiO_4:Eu_z$, wherein $0 \leq x \leq 1$, $0 \leq y \leq 1$ and $0 < z < 1$ is less than about 10µm. Other devices, however, can be prepared with larger grain sizes.

Athough unabsorbed light emitted from the LED contributes to color rendering, unabsorbed light can sometimes escape without mixing with light emitted from the

phosphors, resulting in a reduced overall efficiency of the device. Thus, in one embodiment, the LED and composition are positioned within a reflector cup. A reflector cup can be any depression or recess prepared from a reflecting material. By positioning the LED and phosphor particles in a reflector cup, unabsorbed/unmixed LED-emitted light can be reflected either back to the phosphor particles to eventually be absorbed, or mixed with light emitted from the phosphors.

Fig. 5 shows a schematic view of the device of the present invention. The device comprises LED 1. LED 1 is positioned in a reflector cup 2. LED 1 emits light in a pattern. A phosphor composition 4,5, is positioned in the pattern. The phosphor composition is embedded in a resin 3. In this example, reflector cup 2 can modify light pattern if light is reflected into a space not previously covered by the initial light pattern (e.g. in the case of a parabolic reflector). It is understood that one of ordinary skill in the art can provide reflector cup 2 in any shape that optimizes reflection of light back to phosphor composition 4,5, or optimizes positioning of LED 1 to provide a light pattern for efficient conversion. For example, the walls of reflector cup 2 can be parabolic.

Another aspect of the present invention provides an alternative design to a green LED. Green LEDs have been developed only recently. Current green LEDs, however, are notoriously more inefficient than blue LEDs. In addition, emitted radiation from green LEDs exhibits wavelength shifts with an increase in temperature, which is an undesired characteristic.

Thus, this aspect of the present invention provides a device comprising a green phosphor and a blue light emitting diode, for providing an excitation radiation to the phosphor. By taking advantage of down-conversion, the blue light can be converted to green light via the green phosphor. This device is comparable to a green LED yet eliminates the disadvantages of green LEDs, such as providing comparable efficiencies to blue LEDs and minimizing radiation energy shifts with increasing temperature. In one embodiment, the green phosphor is $(Ba_{1-x-y-z}Sr_xCa_y)_2SiO_4:Eu_z$, wherein $0 \leq x \leq 1$, $0 \leq y \leq 1$ and $0 < z < 1$.

High luminous equivalents values of 575 lm/W can be achieved with this phosphor at a maximum wavelength of about 535 nm, which is far superior to any other green LED or alternative. High absorption of the excitation radiation is preferred to eliminate a significant amount of blue radiation which may spoil efficiency and/or color saturation.

The function and advantage of these and other embodiments of the present invention will be more fully understood from the examples below. The following examples

are intended to illustrate the benefits of the present invention, but do not exemplify the full scope of the invention.

Example 1:

Preparation of $(Ba_{0.49}Sr_{0.49})_2SiO_4:Eu_{0.02}$

15.00 9 (76.01 mmol) BaCO3, 11.22 (76.01 mmol) SrCO3, 0.546 (1.55 mmol) EU203, and 4.80 9 (79.90 mmol) SiO2 are suspended in ethanol. The solvent is slowly evaporated under stirring and NH4Cl is subsequently added to the dried powder. After the material has been thoroughly ground in an agate mortar, the material is filled into alumina crucibles and fired at 600°C for 0.5 h. The powder is ground again and the obtained powder is annealed at 1100 to 1200°C for 4 h under N2/H2. Cooling down to room temperature occurs under N2/H2. Finally, the powder is milled and sieved through a 36 μm sieve.

The spectroscopic properties of $(Ba_{0.49}Sr_{0.49})_2SiO_4:Eu_{0.02}$,prepared this way, are : QE_{460nm} of 70%, Abs_{460nm} of 80%, LE of 483 [lm/W] and colour point x = 0.24, y = 0.65.

Example 2:

White LED comprising $(Ba_{0.49}Sr_{0.49})_2SiO_4:Eu_{0.02}$ and $Sr_2Si_5N_8:Eu$.

A phosphor blend comprising $(Ba_{0.49}Sr_{0.49})_2SiO_4:Eu_{0.02}$ and $Sr_2Si_5N_8:Eu$ is suspended in silicone monomer oil and a droplet of the suspension is deposited onto an InGaN die. A catalyst is added to the silicone monomer to start the polymerization process, resulting in hardening of the silicone. Finally, the LED is sealed with a plastic cap.

Example 3:

White LED comprising $(Ba_{0.49}Sr_{0.49})_2SiO_4:Eu_{0.02}$ and SrS:Eu

A phosphor blend comprising $(Ba_{0.49}Sr_{0.49})_2SiO_4:Eu_{0.02}$ and SrS:Eu is suspended in silicone monomer oil and a droplet of the suspension is deposited onto an InGaN die. A catalyst is added to the silicone monomer to start the polymerization process, resulting in hardening of the silicone. Finally, the LED is sealed with a plastic cap.

CLAIMS:

1. A light emitting device comprising a LED for emitting a pattern of light and a phosphor composition comprising a phosphor of general formula $(Ba_{1-x-y-z}Sr_xCa_y)_2SiO_4:Eu_z$, wherein $0 \leq x \leq 1$, $0 \leq y \leq 1$ and $0 < z < 1$.

2. The light emitting device according to claim 1, wherein the light emitting device has an emission at a wavelength from 450 nm to 480 nm.

3. The light emitting device according to claim, wherein the phosphor composition is comprised in a thin film layer.

4. The light emitting device according to claim 1, wherein the LED is a blue-emitting LED.

5. The light emitting device according to claim 1, wherein the phosphor composition comprises a green phosphor of general formula $(Ba_{1-x-y-z}Sr_xCa_y)_2SiO_4:Eu_z$, wherein $0 \leq x \leq 1$, $0 \leq y \leq 1$ and $0 < z < 1$ and a red phosphor.

6. The light emitting device according to claim 5, wherein the red phosphor is selected from the group of $(Sr_{1-x-y}Ba_xCa_y)S:Eu$ wherein $0 \leq x < 1$ and $0 \leq y < 1$; CaS:Ce,Cl; $Li_2Sr\ SiO_4:Eu$; $(Sr_{1-x}Ca_x)SiO_4:Eu$ wherein $0 \leq x < 1$; $(Y_{1-x}Gd_x)_3(Al_{1-y}Ga_y)_5O_{12}:Ce$ wherein $0 \leq x < 1$ and $0 \leq y < 1$ and $(Sr_{1-x-y}Ba_xCa_y)_2Si_5N_8:Eu$ wherein $0 \leq x < 1$ and $0 \leq y < 1$.

7. The light emitting device according to claim 1, wherein the device is a lamp.

8. The light emitting device according to claim 1, wherein the device is a traffic sign.

9. A phosphor composition comprising a phosphor of general formula

$(Ba_{1-x-y-z}Sr_xCa_y)_2SiO_4:Eu_z$, wherein $0\ \ x\ 1$, $0\ \ y\ \ 1$ and $0 < z < 1$.

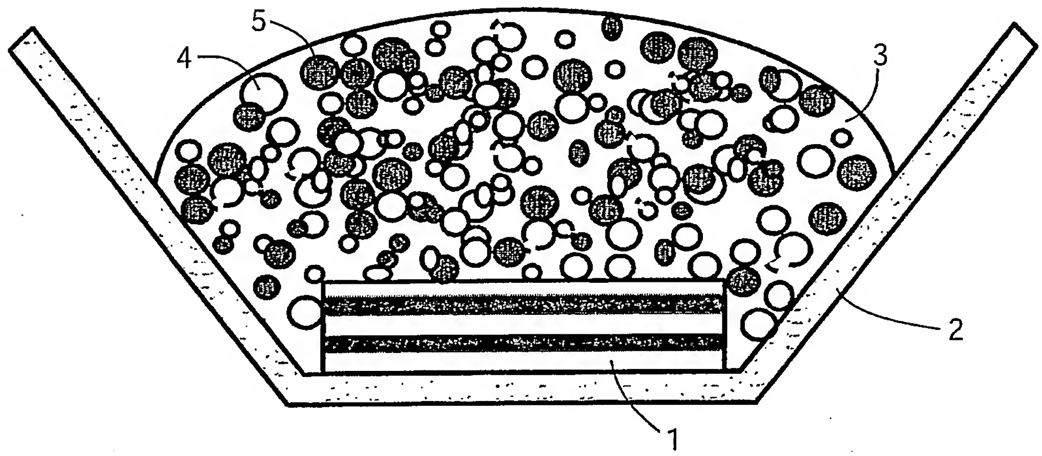


FIG.1

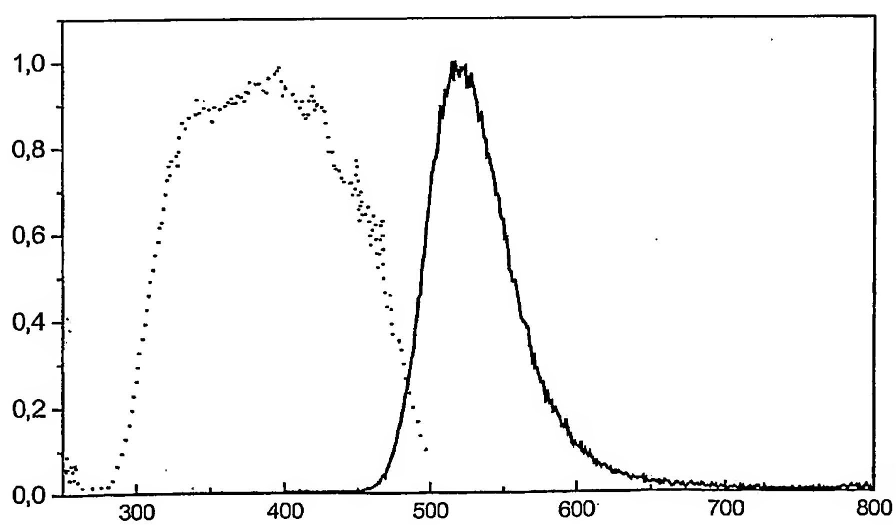
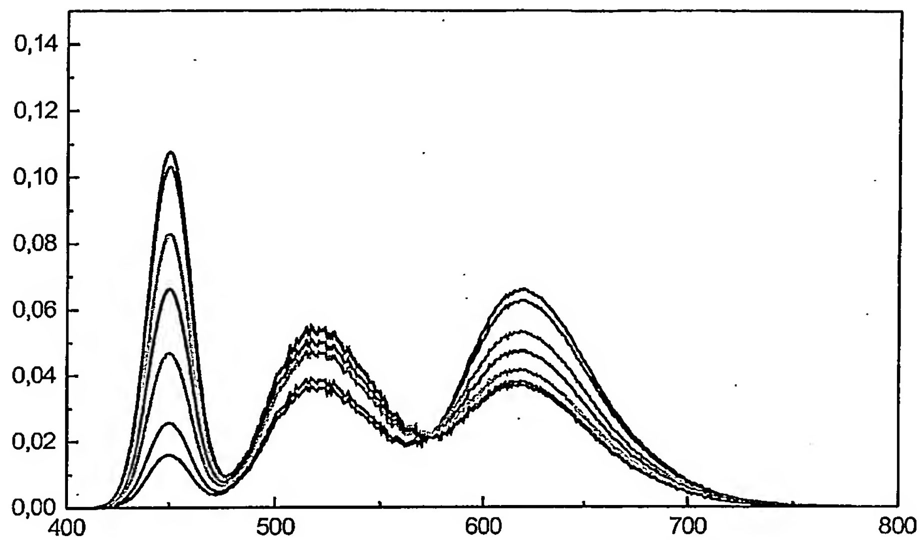


FIG.2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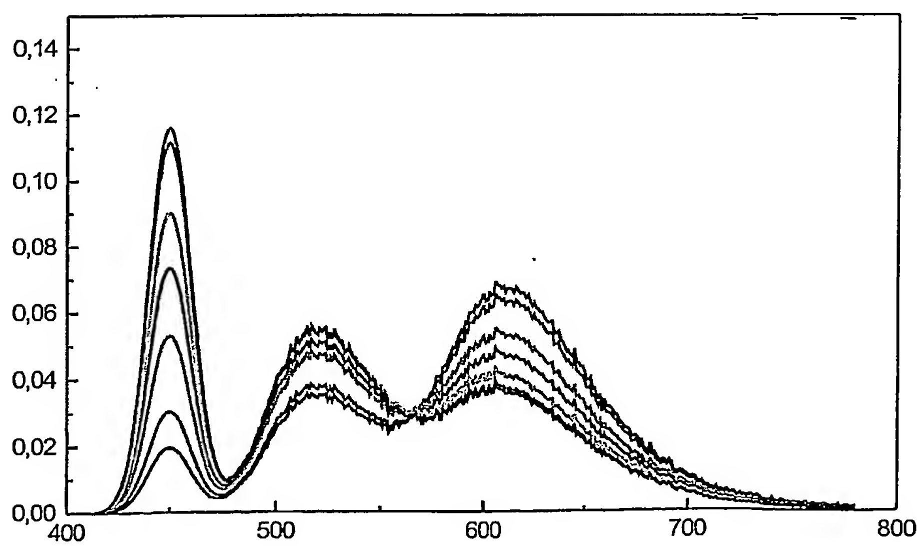
0,04
0,02
0,00
400
500
600
700
800

FIG.3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0,06
0,04
0,02
0,00
400
500
600
700
800

FIG.4

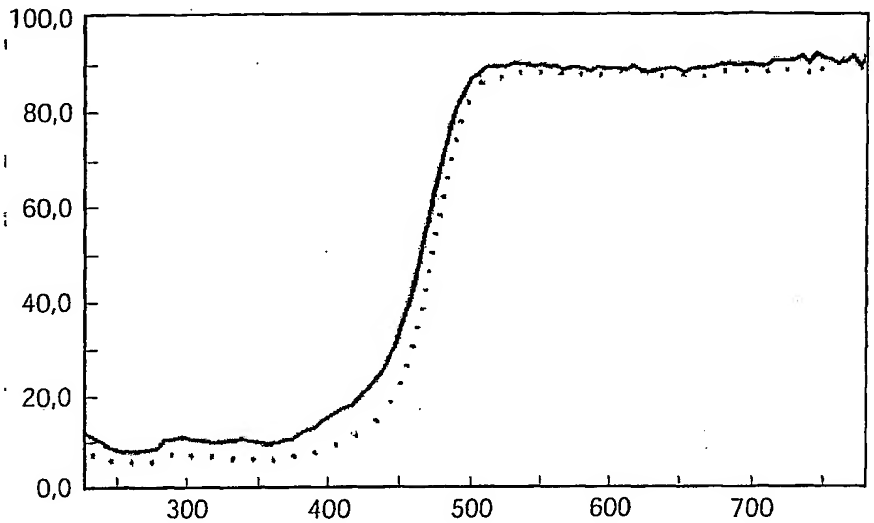

FIG.5

INTERNATIONAL SEARCH REPORT

International Application No
PCT/IB 03/01042

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09K11/08 C09K11/46

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, COMPENDEX, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 180 029 B1 (KODAS TOIVO T ET AL) 30 January 2001 (2001-01-30) table 1 claims 119-123	1-4,7-9
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Y	EP 1 104 799 A (PATRA PATENT TREUHAND) 6 June 2001 (2001-06-06) figures examples	5,6

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
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"P" document published prior to the international filing date but later than the priority date claimed

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
21 July 2003	30/07/2003
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Doslik, N

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/IB 03/01042

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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